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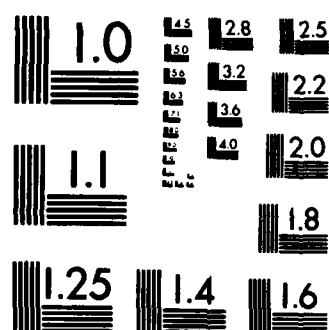
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TECHNICAL REPORT ARLCD-TR-84007

**THE CRYSTAL AND MOLECULAR STRUCTURE REFINEMENT OF
1,2,3-TRIAMINOGUANIDINIUM CHLORIDE**

AD-A142 824

A. J. BRACUTI

JUNE 1984



U.S. ARMY ARMAMENT RESEARCH AND DEVELOPMENT CENTER

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Triaminoguanidinium chloride TAG TAG salts Crystal structure Molecular structure		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The crystal structure of triaminoguanidinium chloride (TAGCl) was refined using three dimensional x-ray diffraction data. The hexagonal structure (P6(3)/m) has unit-cell dimensions: a=b=7.480(1) A and, c=6.218(1) A. The structure consists of layers of ions parallel to (00l) located at $\pm \frac{1}{2}c$ held together by van der Waals forces. The C-N bond length is 1.325(2) A and the N-N bond length is 1.411(4) which agree quite well with the bond lengths found in triaminoguanidinium nitrate (TAGN).		

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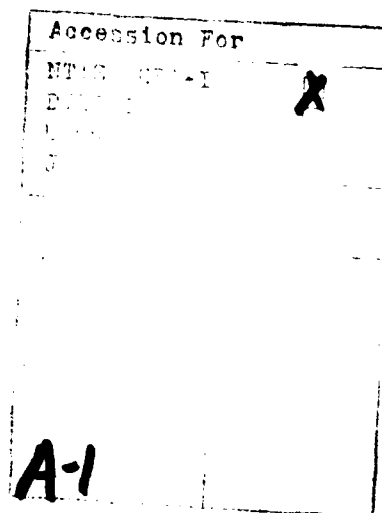
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INTRODUCTION

Triaminoguanidinium chloride (TAGCl) was the starting material used in an ion exchange method reported by Picard, Satriana, and Masuelli (ref 1) for the preparation of a triaminoguanidinium nitrate (TAGN) sample used in the crystal and molecular structure determination reported by Bracuti (ref 2).

In an x-ray diffraction investigation of TAGCl using a limited number of two-dimensional data, Okaya and Pepinsky (ref 3) reported a layered hexagonal structure ($P6_3/m$) with lattice parameters $a = 7.528$ and $c = 6.253$ Å, in which TAG cations displayed C_{3h} symmetry (fig. 1) with C-N and N-N bond lengths of 1.318(9) and 1.450(14) Å, respectively. While in the TAGN structure determination using three-dimensional diffraction data, TAGN also formed a layered structure but in the orthorhombic system ($Pbcm$). In this case the TAG cation approximates C_{3h} symmetry, with somewhat longer C-N bond lengths of 1.324(6), 1.324(6), and 1.318(5) Å (mean 1.322(6) Å); and significantly shorter N-N bond lengths of 1.415(6), 1.407(5), and 1.397(5) Å (mean 1.406(5) Å). In a later neutron diffraction crystal structure refinement of TAGN, Choi and Prince (ref 4) also reported longer C-N bond lengths of 1.332(3), 1.324(4), and 1.336(4) Å (mean 1.331(4) Å); and significantly shorter N-N bond lengths of 1.411(9), 1.401(5), and 1.396(4) Å (mean 1.403(6) Å).

In view of the disagreement in the reported N-N bond lengths and the large standard deviations in bond lengths reported by Okaya and Pepinsky, a three-dimensional refinement of the TAGCl crystal structure was undertaken.

EXPERIMENTAL PROCEDURES

From a sample of TAGCl recrystallized from water, a colorless prismatic crystal (0.15 x 0.15 x 0.20 mm) was mounted on a glass fiber with its long axis approximately coaxial with the ϕ axis of the goniometer. Data collection was performed with $CuK\alpha$ x-radiation ($\lambda = 1.54184$ Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal incident beam monochromator.

Lattice parameters obtained using 20 reflections in the range of $18 < \theta < 24^\circ$ were $a = 7.480(1)$, $c = 6.218(1)$ Å with a calculated volume of 301.3 Å³. The calculated density is 1.549 g cm⁻³ as compared to the observed value of 1.550 g cm⁻³.

Intensity data (upper limit $150^\circ 2\theta$) were collected at $23 \pm 1^\circ C$ with the $\omega - \theta$ scan technique on 302 reflections of which 280 were unique. Nineteen reflections were rejected as unobserved because of an imposed constraint $F > 2\sigma(F)$ in which (F) is the standard deviation based on counting statistics. Three representative reflections measured every 25 minutes, in order to check the crystal and electronic stability of the system, yielded constant intensities within experimental error.

The data were corrected for Lorentz and polarization effects. No correction for absorption was attempted. The linear absorption coefficient is 4.92 mm^{-1} . Scattering factors were obtained from Cromer and Waber (ref 5).

The nonhydrogen atomic positions for the trial structure were taken from the Okaya and Pepinsky TAGCl structure while the hydrogen atomic positions were taken from those reported in the TAGN structure determination. An anisotropic refinement was carried out with the full-matrix least squares program FLINUS, a modification of the Oak Ridge fortran least squares (ORFELS) program (Busing, Martin, and Levy, ref 6). The function $\sum w (|F_o| - |F_c|)^2$ was minimized with $w = 1/\sigma^2(F)$. A secondary extinction function, $g = 1.3/0 \times 10^{-5}$, was also refined (Coppens and Hamilton, ref 7) with the crystal mean free path treated as a constant. Refinement of 19 variable parameters (tables 1 and 2) converged with a largest parameter shift of 0.009 times its estimated standard deviation; an R value of 0.049; a weighted R value of 0.074; and a standard deviation of an observation of unit weight of 2.44 (based on 261 observations and 19 parameters varied).

The crystal data are:

Hexagonal space group $P6_3/m$ (no. 176); $a = 7.480(1) \text{ \AA}$, $c = 6.218(1) \text{ \AA}$; $V = 301.3 \text{ \AA}^3$, $Z = 2$; $D_x = 1.550 \text{ g cm}^{-3}$, $D_o = 1.549 \text{ g cm}^{-3}$; molecular weight 140.57; $F(000) = 148$; $\mu = 4.92 \text{ mm}^{-1}$; chemical formula $C(NH)_3(NH_2)_3Cl$; $T = 296(1) \text{ K}$; $R = 0.049$; 280 unique reflections, systematic absence $l = 2n + 1$ for $00l$.

DISCUSSION

With the exception of the amino hydrogen atoms, all atoms in this structure lie in two parallel mirror planes at $\pm 1/4c$ (figs. 2 and 3). The planar TAG cations are stacked directly over each other in adjacent layers 3.109 \AA apart (table 3); while the chloride anions are stacked in alternate layers 6.218 \AA apart. This packing arrangement generally corresponds to that found in TAGN in which the TAG cations are in adjacent layers 3.272 \AA , and the central nitrogen atom and one oxygen atom of each nitrate anion are in alternate layers 6.543 \AA apart.

The closest interionic contacts between layers occur among the amino groups of the TAG cations and the chloride ions. The closest distance between an amino hydrogen atom and a chloride ion ($H(2)-Cl^-$) is 2.98(3) \AA and the distance between the amino nitrogen atom and a chloride ion ($N(2)-Cl^-$) is 3.684(2) \AA with an interatomic angle ($N(2)-H(2)-Cl^-$) of $149^\circ(3)$. Although this interatomic distance is shorter than the 3.692 \AA previously reported by Okaya and Pepinsky, it is still longer than would be observed if hydrogen bonding were involved. As a result, only van der Waal and coulombic forces operate between layers in contrast to TAGN in which there is also interlayer hydrogen bonding between one amino group and the nitrate ion.

With any layer (fig. 4), each chloride anion is surrounded by three TAG cations and is hydrogen bonded to three equivalent nearest-neighbor guanidinium nitrogen atoms with a nitrogen atom to chloride ion distance ($N(1)-Cl^-$) of 3.158(3) Å, a hydrogen to chloride ion distance ($H(1)-Cl^-$) of 2.43 Å; and a bond angle ($N(1)-H(1)-Cl^-$) of $144(4)^\circ$. Each chloride ion also has three equivalent nearest neighbor amino groups with three pair of hydrogen atoms ($H(2)-Cl^-$) at a distance of 3.14(3) Å and three nitrogen atoms ($N(2)-Cl^-$) at a distance of 3.579(3) Å.

Each TAG cation maintains strict C_{3h} symmetry because the central carbon atom is located on a six-fold inversion axis (6) which is normal to the plane of the cation. These symmetry constraints produce three identical C-N bonds (1.325(2) Å) and three identical N-N bonds* (1.411(4) Å) which agree with the mean C-N and N-N bond lengths found in TAGN. These results are consistent with the resonance hybrid model (proposed by Okaya and Pepinsky) for the TAG cation ion in which three C-N bonds are partial double bonds.

* This is not to imply an a priori symmetry dependence. Actually, the observed molecular symmetry is a consequence of the chemical bonding.

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Table 1. Atomic coordinates and equivalent isotropic temperature factors and their standard deviations

Atoms	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>Beq</u>
C	0.0	0.0	0.25	2.89(1)
N(1)	0.1864(4)	0.1660(4)	0.25	3.16(9)
N(2)	0.2035(5)	0.3626(5)	0.25	3.86(9)
H(1)	0.291(7)	0.150(6)	0.25	4(1)
H(2)	0.261(6)	0.405(5)	0.362(4)	4.8(7)
Cl	0.6667	0.3333	0.25	3.51(6)

Table 2. Selected interatomic distances (Å) and angles (°) and their standard deviations

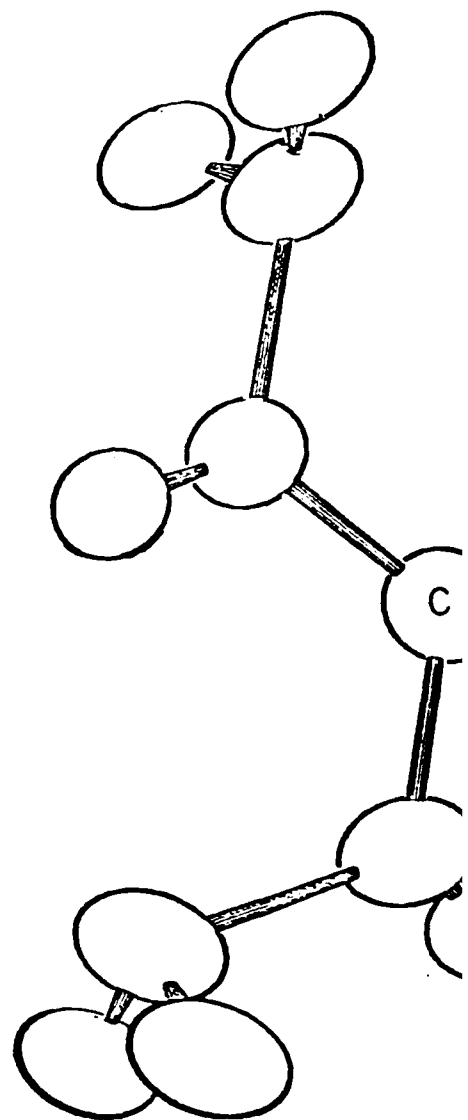
<u>Interatomic distance, Å</u>		<u>Interatomic angle, °</u>	
C-N(1)	1.325(2)	N(1)-C-N(1)	120.0
N(1)-N(2)	1.411(4)	C-N(1)-N(2)	118.8(2)
N(1)-H(1)	0.85(5)	C-N(1)-H(2)	119(3)
N(2)-H(2)	0.79(3)	N(1)-N(2)-H(2)	100(2)
N(1)-Cl	3.158(3)	H(2)-N(2)-H(2)	122(5)
N(2)-Cl	3.579(3)	N(1)-H(1)-Cl	144(4)
N(2)-Cl*	3.684(2)	N(2)-H(2)-Cl	97.4(6)
H(1)-Cl	2.43(5)	N(2)-H(2)-Cl*	149(3)
H(2)-Cl	3.41(3)		
H(2)-Cl*	2.98(3)		
C-C	3.109(1)		

* Cl ion at $\frac{3}{4}$ c.

rs* and their standard deviations

<u>3</u>	<u>β_{12}</u>	<u>β_{13}</u>	<u>β_{23}</u>
(10)	0.0080(10)	0	0
(8)	0.0068(4)	0	0
(9)	0.0093(5)	0	0
22)	0.012(10)	0	0
8)	0.031(10)	0	0
(5)	0.0064(3)	0	0

$$-2hk\beta_{13} + 2k\beta_{23})$$



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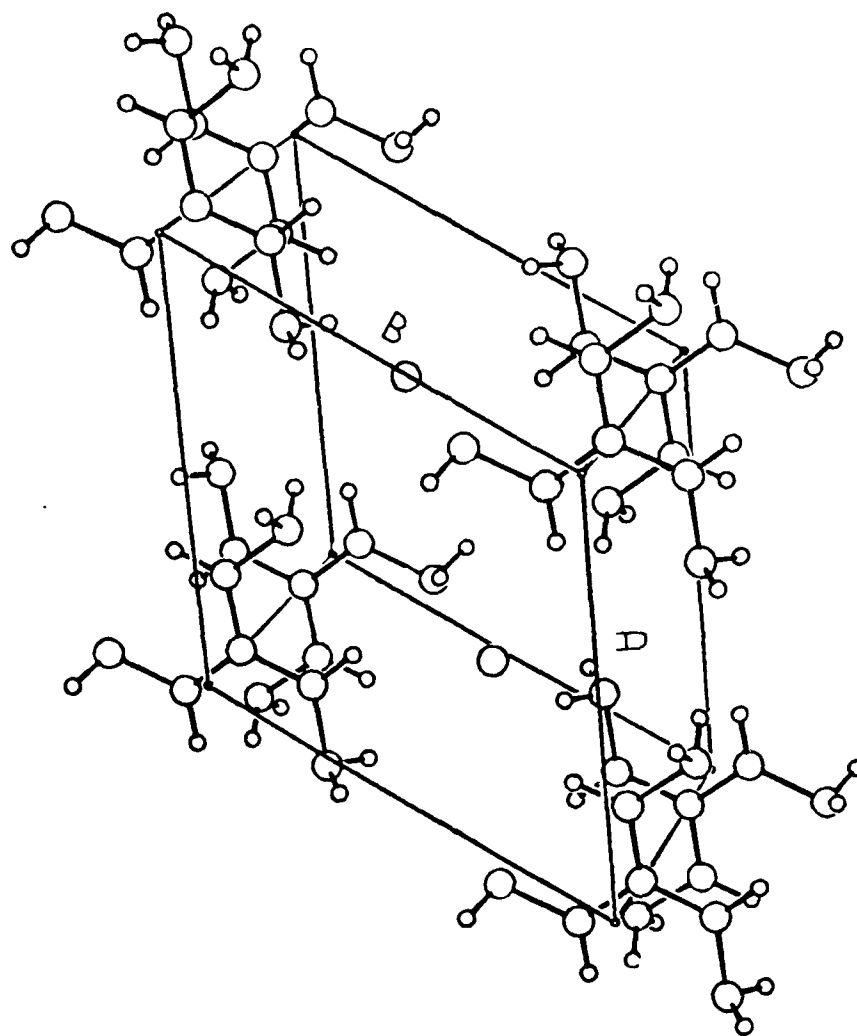


Figure 2. Unit cell of TAGCl viewed down c axis

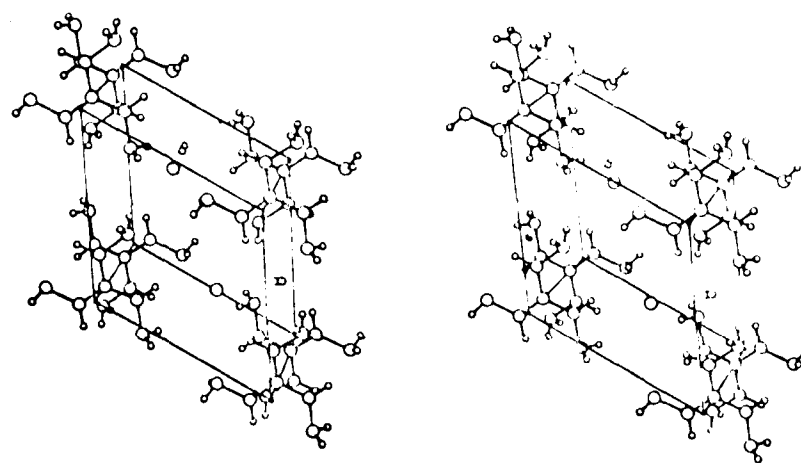


Figure 3. Stereo view of TAGCl unit cell viewed down c axis

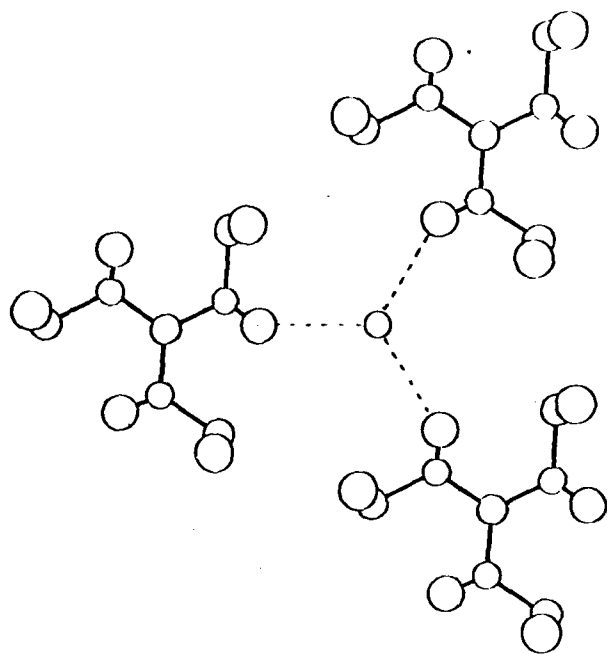


Figure 4. Ionic packing in single layer with hydrogen bonds designated by dashed lines

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